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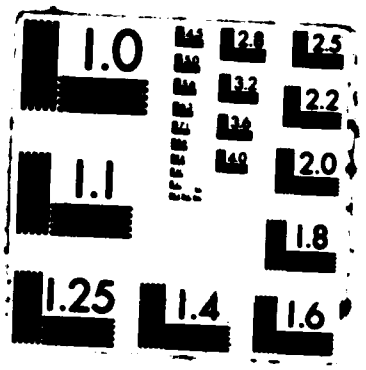
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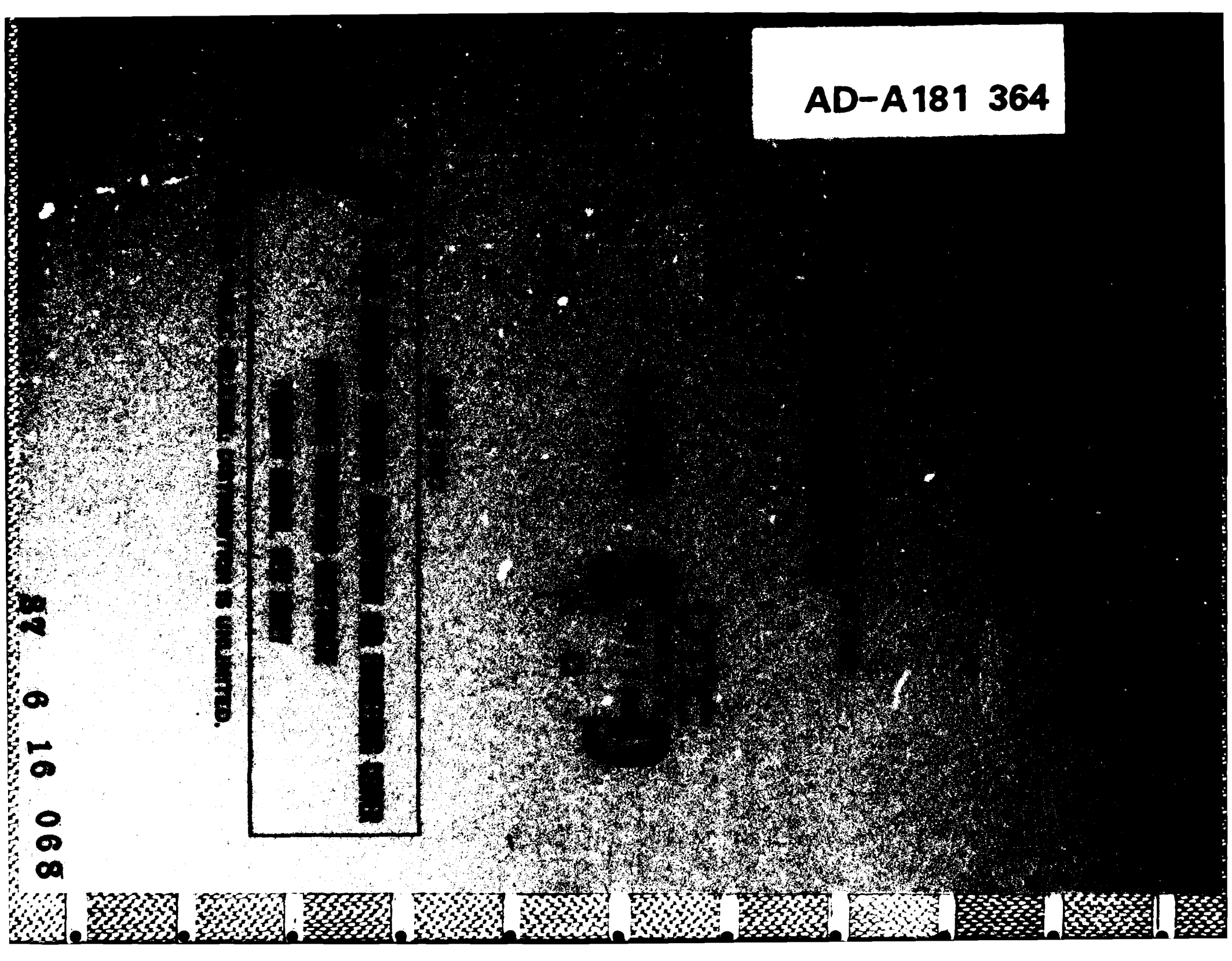
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1. REPORT NUMBER: TECHNICAL REPORT ARAED-TR-87019	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER: AD-A181 364	
4. TITLE (and Subtitle): THE ISOLATION OF THE FREE-BASE OF THE TRIAMINOGUANIDINIUM ION	5. TYPE OF REPORT & PERIOD COVERED
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): A. J. Bracuti C. Y. Manning	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: ARDEC, AED Energetics and Warheads Div (SMCAR-AEE) Picatinny Arsenal, NJ 07806-5000	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: ARDEC, IMD STINFO Div (SMCAR-MSI) Picatinny Arsenal, NJ 07806-5000	12. REPORT DATE: June 1987 13. NUMBER OF PAGES: 10
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Free base,
Triaminoguanidine,
Triaminoguanidinium hydroxide,
Preparation,
Isolation,
Cation exchange,
guanidine
amino acids

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A non-aqueous cation exchange method was developed for the preparation and isolation of the highly air-sensitive free-base of the triaminoguanidinium ion. Elemental analysis performed on the free-base indicated its composition was triaminoguanidine rather than triaminoguanidinium hydroxide.

Keywords:

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INTRODUCTION

This report describes the preparation and isolation of the free-base of the triaminoguanidium ion (TAG). Is it triaminoguanidine (TAG) or is it triaminoguanidinium hydroxide (TAGOH)? Although little is known about this base itself, it is frequently shown as an intermediate in reaction schemes or as a starting material for syntheses of selected TAG salts. For example, in an anion exchange method developed for the production of the nitrate salt (TAGN), the base is the required intermediate (ref 1).

$$\text{TAGCL} + \text{R OH} \longrightarrow \text{free-base} + \text{R H} + \text{H2O} \qquad (1)$$

$$\text{free-base} + HNO_3 \longrightarrow \text{TAGN} + H_2O \qquad (2)$$

In reaction (1), there is an exchange between the hydroxyl ions (OH^-) on the exchange resin (R OH) with the chloride ions (Cl^-) of the salt triaminoguanidinium chloride (TAGCl). This suggests that the eluted base might be an aqueous solution of triaminoguanidinium hydroxide (TAGOH).

There is also a suspicion that the highly reactive base produced by the hydrolysis of any TAG salt is probably the primary cause for the occasional discoloration of TAGN and the ultimate erratic behavior sometimes observed with propellants containing TAGN (ref 2 and 3).

Therefore, the rationale behind this effort was twofold: 1) To prepare or isolate the free-base; 2) To chemically identify the free-base.

EXPERIMENTAL

The free-base was prepared by means of the following nonaqueous cationic exchange method:

1. Initially, an aqueous solution of a TAG salt (TAGN, in this case) was eluted slowly through a lightly cross-linked strong cation exchange resin (e.g., Amberlite 118) which was charged with hydrogen ions (R H).

$$\text{R H} + \text{TAGX} \longrightarrow \text{R TAG} + \text{HX} \qquad (3)$$

2. To determine the quantity of TAG cations loaded onto the exchange column, the eluted acid (HX) was titrated with standard base (NaOH) to a ph of 4.

3. Upon completion of the cation exchange, the column was rinsed with deionized water until the effluent wash water had a ph of 7.

4. The interstitial water in the column was then displaced with oxygen-free methanol (de-aerated with nitrogen).

5. The free-base was then eluted from the column with an oxygen-free methanolic solution of sodium hydroxide (NaOH) into an inert liquid hydrocarbon (iso-octane) which acted as a protective barrier against oxidation by air

R TAG + NaOH ------> R Na + free-base (4)

6. Overnight refrigeration of the effluent resulted in crystallization of the free-base.

7. The crystals were dried in vacua and stored under dried nitrogen to prevent oxidation.

8. At this point, the chemical identity of the free-base was still uncertain. Was it TAG or TAGOH?

RESULTS

The reaction product consisted of small white acicular crystals which rapidly discolored when exposed to air. The initial color was a pale pink, which gradually changed to a more intense rose-violet shade.

Elemental analysis (table 1) of 2.5-mg samplings indicated that the sample contained 11.62% carbon, 79.8% nitrogen, 7.62% hydrogen, and 0.81% oxygen. Theoretically, pure TAG contains 11.53% carbon, 80.71% nitrogen, 7.76% hydrogen, and 0.00 oxygen.

The molecular formula based upon the elemental analysis is $C_{19}N_{11}H_{15}O$ or $CN_6H_8O_{0.05}$ which corresponds to neither TAG (CN_6H_8) nor TAGOH ($CN_6H_{10}O$). However, if one assumes that oxygen is present only because of inadvertent air oxidation of TAG to form CN_4H_6O (DAU, diaminourea or sometimes called carbazide), then the sample should be a mixture of TAG and DAU. Since only one atom of oxygen is found in the molecular formula of the sample, this suggests, based on molecular formulas of both TAG and DAU, that the batch sample is a mixture containing 95% TAG and 5% DAU.

CONCLUSIONS

A satisfactory method for synthesizing and isolating the free-base of TAG salts has been devised. Although some oxidation impurity was found in the sample, this probably can be avoided by exercising more scrupulous laboratory precautions.

The results of this effort also suggest that similar methods could be devised for the preparation of other reactive and nonreactive TAG salts.

Elemental analysis indicated that the anhydrous form of the free-base is triaminoguanidine (CN_6H_8) rather than triaminoguanidinium hydroxide.

RECOMMENDATIONS

A single crystal x-ray diffraction determination of the molecular structure of the free-base should be undertaken in order to confirm that it is actually triaminoguanidine.

Other reactive TAG salts such as the azide should be prepared by this method.

Table 1. Element analysis results

Element, Wt. (%)	Free-base sample	TAG* CH_6H_8	TAGOH* $CN_6H_{10}O$	DAU CN_4H_6O
Carbon	11.62	11.53	39.36	13.33
Nitrogen	79.80	89.71	46.52	62.22
Hydrogen	7.62	7.76	5.43	6.66
Oxygen	0.81	0.0	8.79	17.71

*Calculated values based on molecular formula.

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